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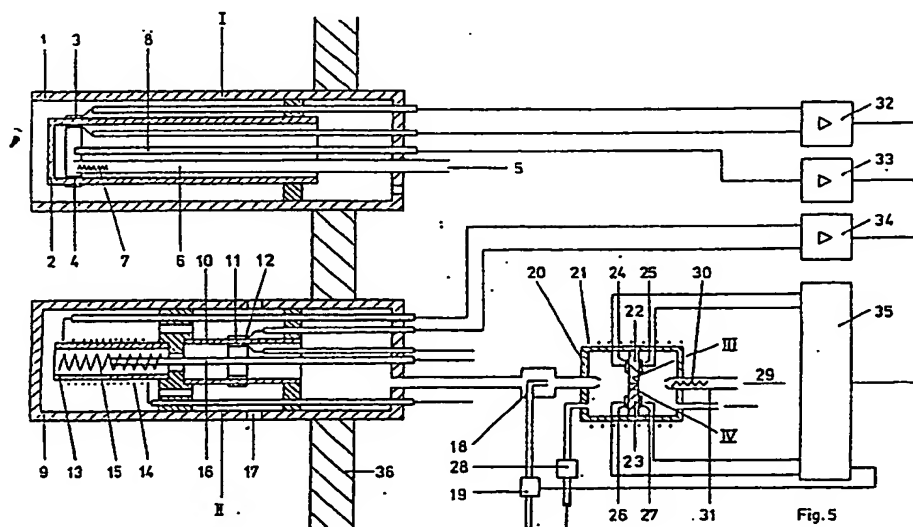
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(54) Arrangement for and method of monitoring heat treatment processes

(57) Heat treatment processes such as gas nitration are monitored by four sensors, preferably of solid electrolyte which determine the status of the gas atmosphere. Gas sensor I in the treatment gas measures the actual oxygen partial pressure in the atmosphere, while the gas sensor II in conjunction with a heated catalyst path 15 supplies a parameter characteristic of the remoteness of the gas phase state from the state of equilibrium. Gas sensor III supplies a value for the level of carbon in the treatment gas and the gas sensor IV provides an auxiliary value for controlling an oxidising gas dispensing arrangement (18) upstream of the gas sensor III to ensure complete oxidation of the gas reaching sensors III and IV. In sensor I the reference gas passes over a catalyst 7 and, sensor II uses either the same reference gas as sensor I (Figure 6) or oxidises the treatment gas in heated catalyst 15 to form the reference gas. Temperature measurement, and heating of the sensors is provided.



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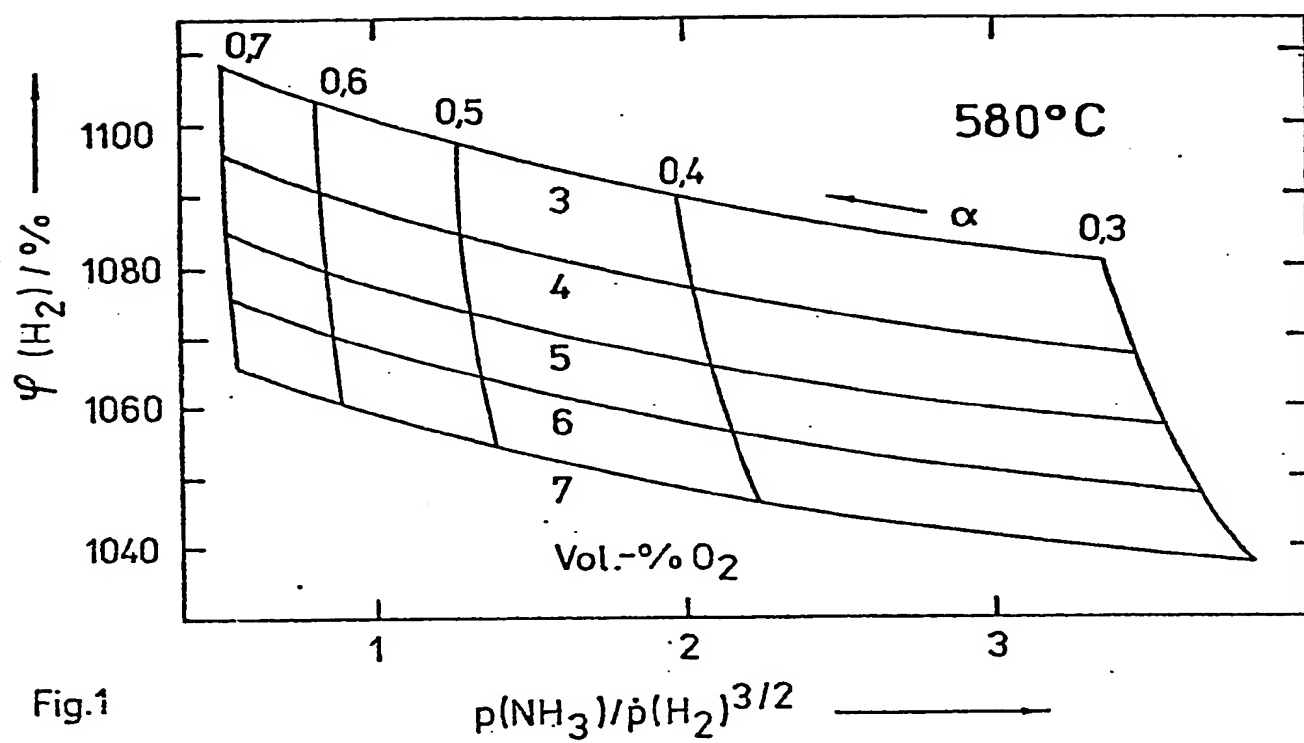


Fig.1

 $p(\text{NH}_3)/p(\text{H}_2)^{3/2}$

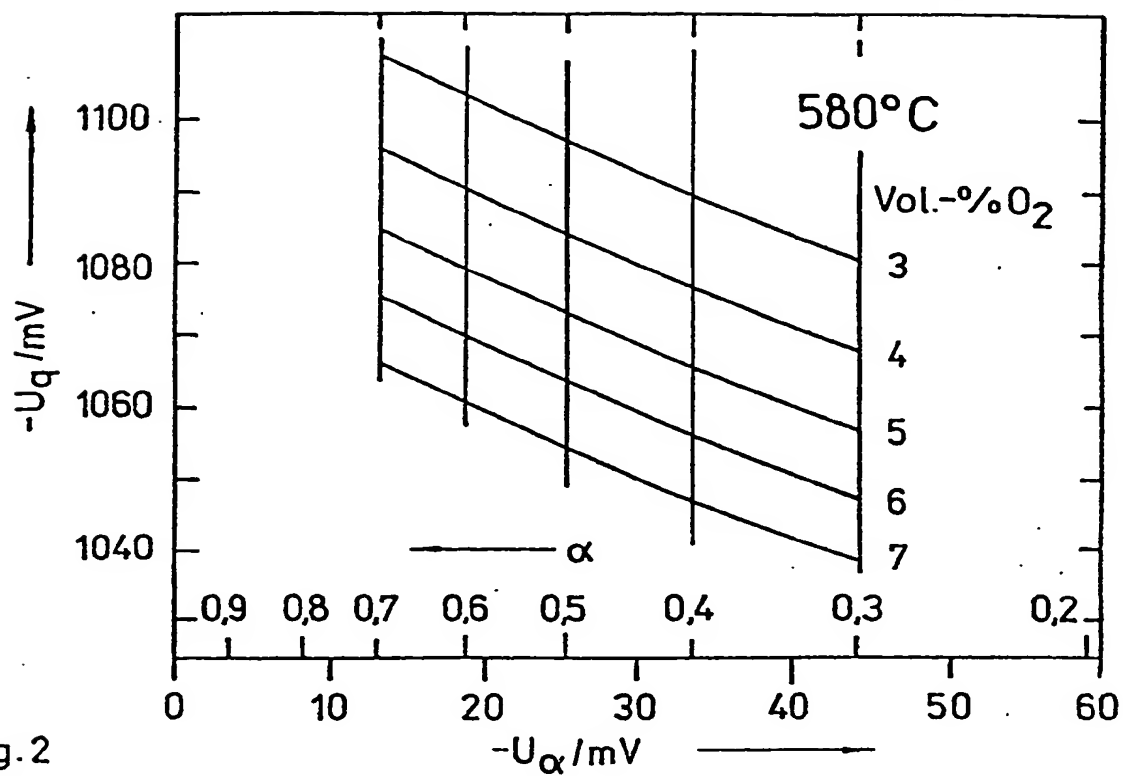


Fig. 2

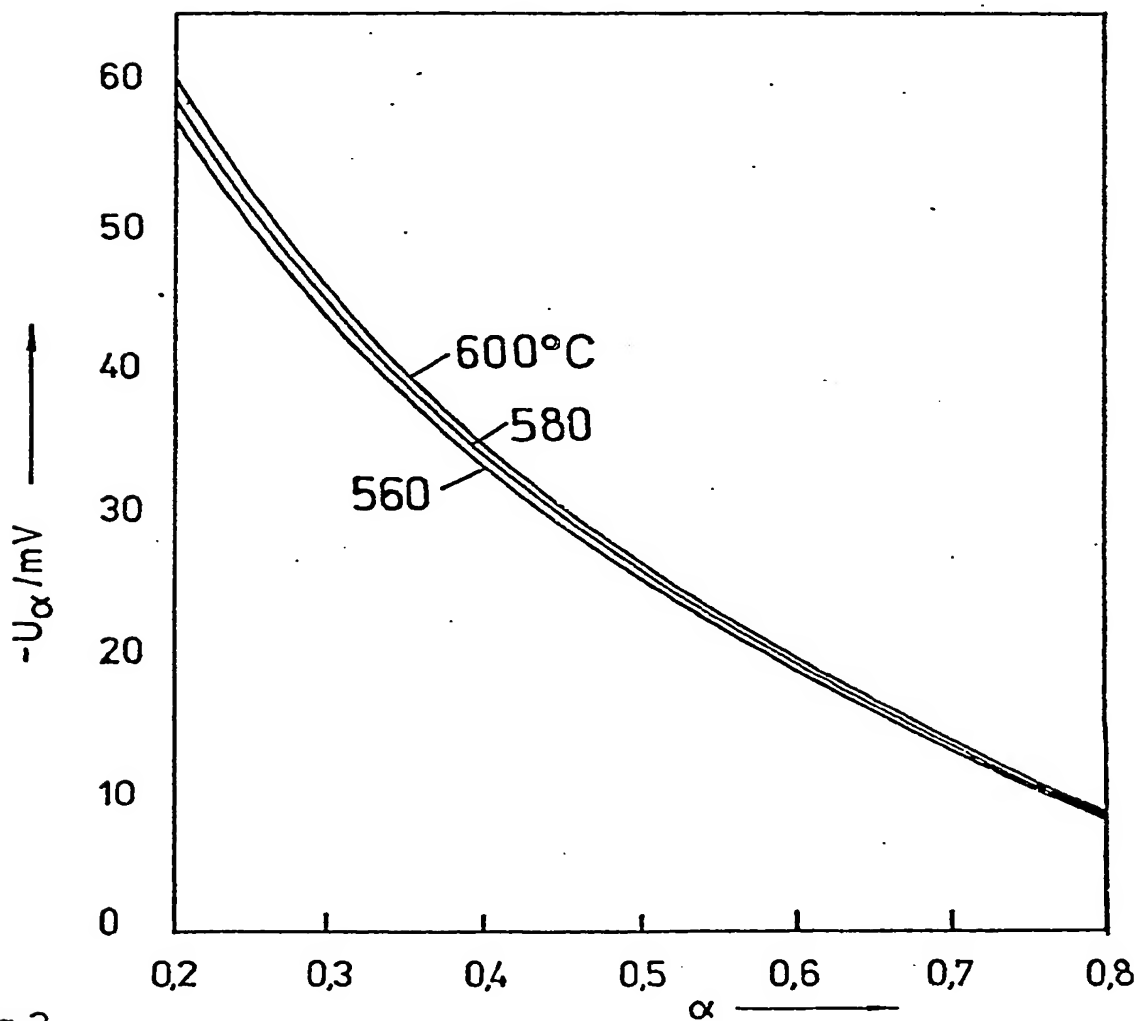


Fig. 3

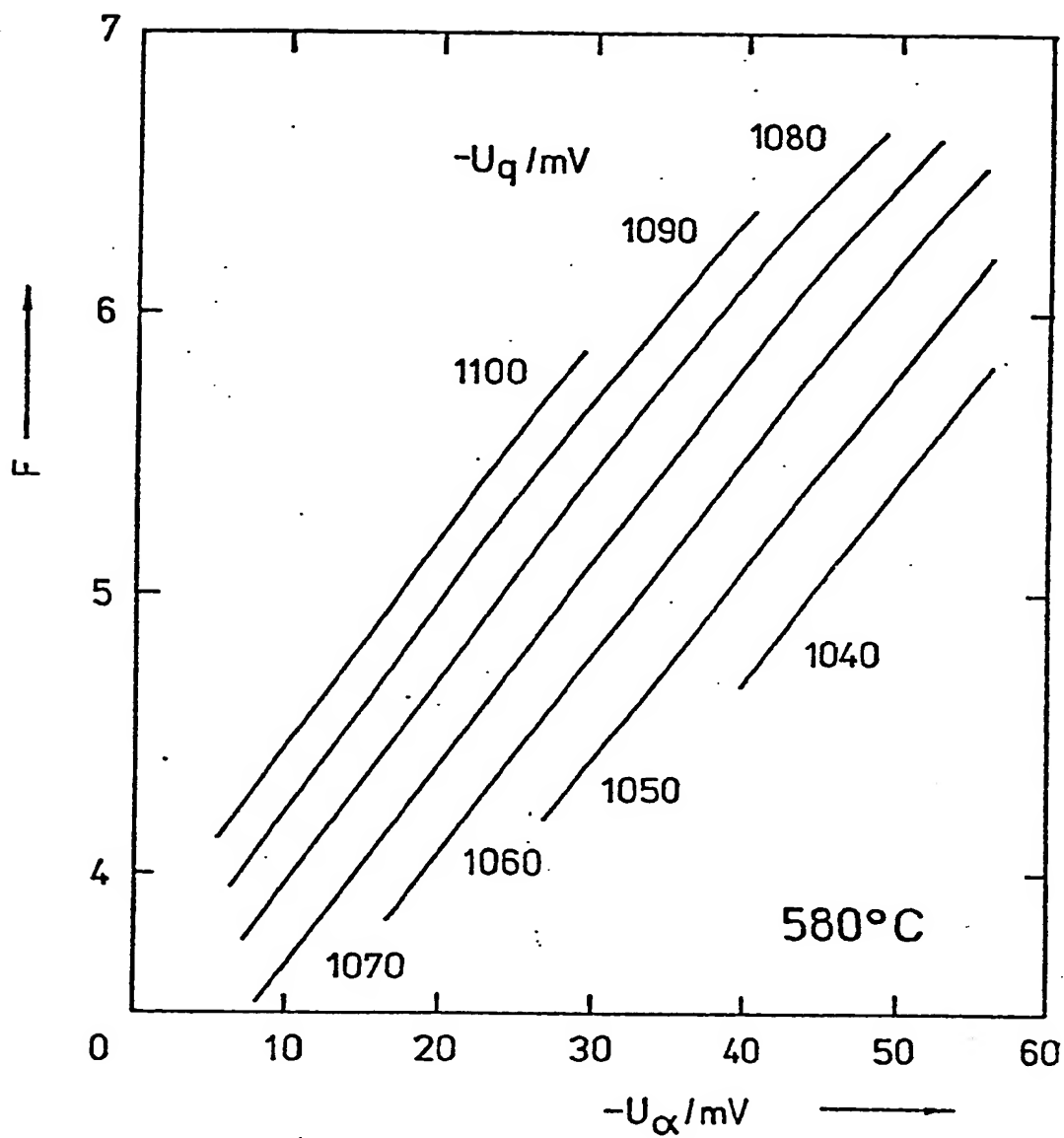


Fig. 4

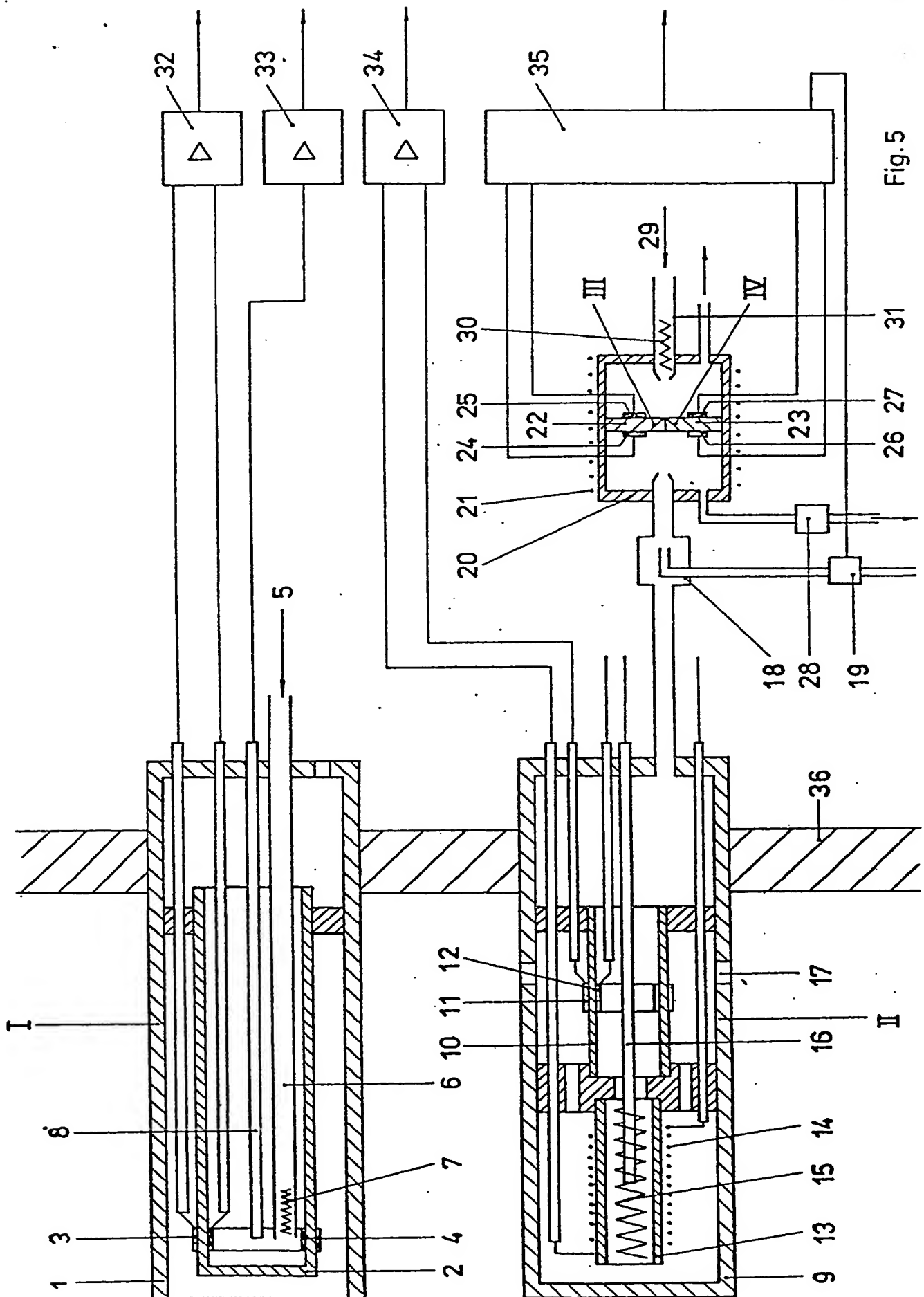


Fig. 5

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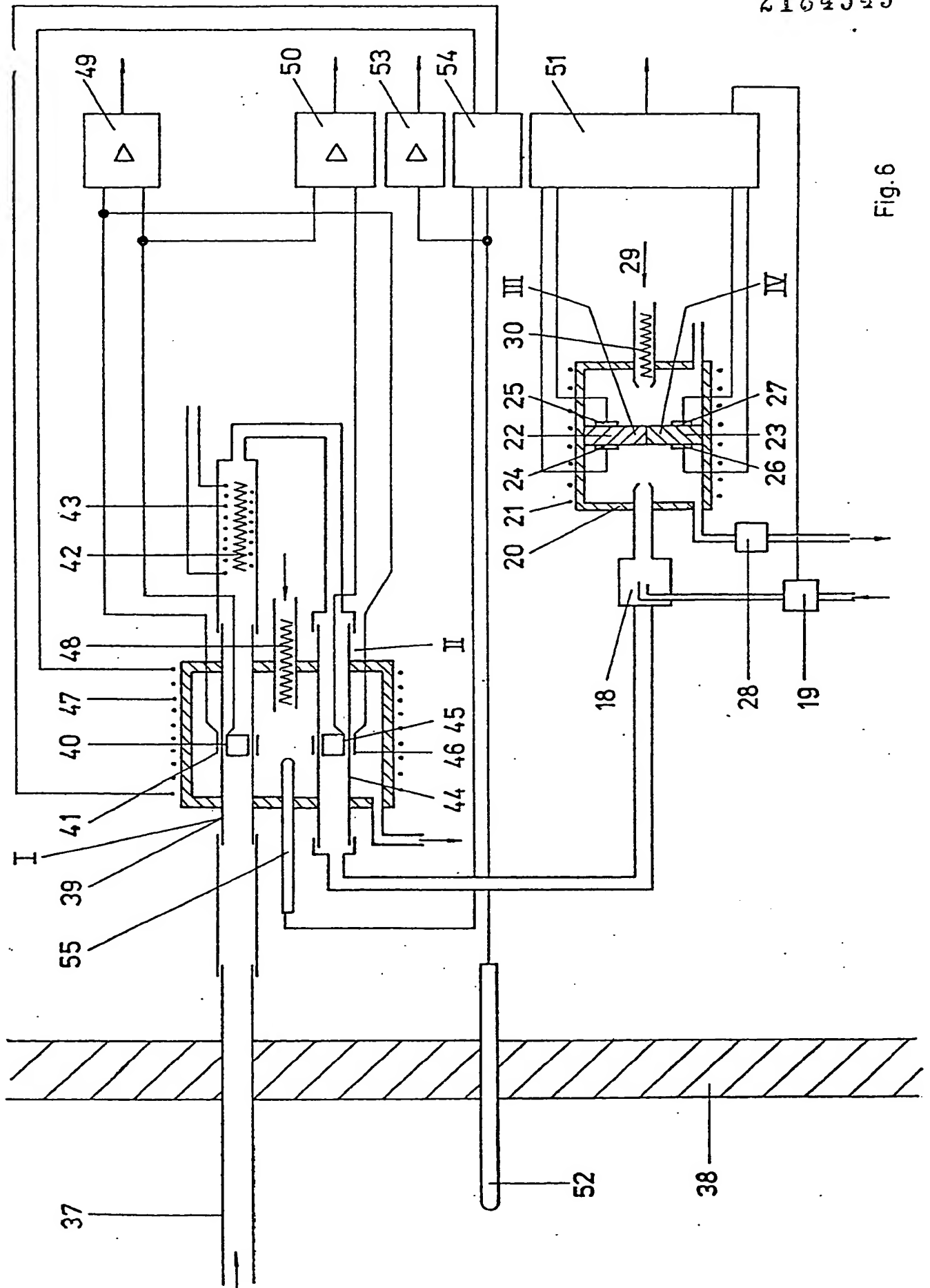


Fig. 6

SPECIFICATION

Arrangement for and method for monitoring heat treatment processes

- 5 The invention relates to an arrangement and a method of applying the arrangement for monitoring heat treatment processes such as gas nitration, gas oxynitration, gas carbonitration and gas oxycarbonitration, along with carbonitride and nitride hardening with the object of achieving reproducible treatment results at optimised time, energy and material costs. 5
- In order to be able to conduct processes of nitration in gas mixtures under control, it is known that gas analytical methods are needed in order to ascertain characteristic gas situations or components. Since the introduction of gas nitration in dissociated ammonia, a multiplicity of possible ways of ascertaining individual values characteristic of the composition of the nitration atmosphere have been tried out (S. Bohmer et al, Neue Hutte 24 (1974) 10, pp. 384-390). 10
- The simplest and most frequently practised method is the volumetric determination of the degree of dissociation. Methods and apparatus are described in "Chemisch-thermische Oberflächenbehandlung von Stahl", VEB Verlag Technik, Berlin 1953, p. 182. 15
- Using known mathematical relationships, it is possible to determine from the degree of dissociation the partial pressures for ammonia, nitrogen and hydrogen. A disadvantage of this apparatus is its discontinuous operation and the lack of a signal for process control.
- 20 Improved methods and apparatuses are known from S. Dombrovskij et al: Metalloved. obra. met. (1966)8, pp. 52-55; Modulevskij et al: Mechaniz. i. Avtomatiz. Prosv. 24 (1970)8, p. 4; Kolosvari, Z. et al: ZWF 68 (1973)6, p. 304. 20
- As their content, they deal with conversion of the measured value into an electrical magnitude and rapid processing of the measured values. The fundamental above-mentioned disadvantage of volumetric determination of the degree of dissociation, the discontinuous method of operation, is not however overcome. 25
- Continuously operating apparatuses for determining the concentration of individual components in nitrating gas are based on measuring the infra-red absorption in order to determine the proportion of the ammonia volume (T. Bell et al in Source Book on Nitriding, Metals Park, Ohio 1977) or on the measurement of the heat conductivity in the determination of the hydrogen volume proportion (W. Lerche et al, Freiburger 30 Forschungsheft B 185 (1976)). According to this, it is conventional in a mixture of ammonia and air to use a measuring instrument operating on the paramagnetic principle to measure the oxygen concentration and to measure the hydrogen concentration on the heat conductivity principle using a measuring instrument applied to the waste gas from a heat treatment furnace. From the results of measurement, it is possible to calculate the partial pressure ratio $\bar{p}(\text{NH}_3) / \bar{p}(\text{H}_2)^{3/2}$, by varying which it is possible to adjust the ion-nitrogen 35 phases in the marginal layer. 35
- Determining the proportions of volume of ammonia in ammonia-hydrogen volume portions in the hydrogen-ammonia-nitrogen gas mixture is always possible without any problem if there are no further gas components present in the nitrating gas. As soon as an oxidising gas component (for example oxygen, air, carbon dioxide) is added to the starting gas, ammonia, it is no longer possible to achieve a clear relationship 40 between the degree of association and the measured gas component, ammonia or hydrogen. Basically, all parts by volume can be determined by methods and apparatuses used in gas chromatography. Disadvantageous are the high costs of apparatus and personnel as well as the discontinuous manner of operation. 40
- Common to all the previously known apparatuses is the fact that they can only be used for ascertaining the composition of the waste gas. An apparatus for measuring the atmosphere within the furnace is known from 45 I. Lachtin et al: Neue Hutte 22 (1977)6, p. 320. It is based on measuring the ion flow. Only by determining the ammonia ion proportion is it possible to identify the state of dissociation of the ammonia. As soon as an oxidising gas component, for example oxygen, is added to the starting gas, ammonia, it is no longer possible to have an unequivocal relationship between the degree of dissociation and the measured gas component. 45
- 50 Monitoring and conduct of nitration processes cannot be effectively structured by supervisory measures upstream or downstream of the heat treatment furnace, but only by measuring process-determining values directly in the vicinity of the workpiece surface. 50
- Furthermore, hitherto proposed arrangements of solid electrolyte measuring cells failed to bring the necessary success. The arrangements with solid electrolyte measuring probes suggested in DD-PS 222 415 and 55 DD-PS 222 416 neither fulfil the function reliably nor are they suitable for supplying information about the proportion of carbon in the treatment gas. 55
- Although DD-PS 227 802 finds a more suitable solution for a partial function, the catalytic decomposition of the ammonia, the aforementioned defect is not resolved. Hitherto, no apparatus has been indicated which makes it possible to ascertain altogether the parameters required for the conduct of heat treatment processes. 60
- 60 The invention is based on the problem of indicating an arrangement for monitoring heat treatment processes such as gas nitration, gas oxynitration, gas carbonitration and gas oxycarbonitration as well as for carbonitration and nitride hardening, indicating for the purpose a method of monitoring the status of the gas atmospheres with this arrangement.
- 65 The solution to the problem is viewed in an arrangement consisting of four gas sensors, preferably solid 65

electrolyte sensors. In a first embodiment, the arrangement consists of two closely adjacently mounted solid electrolyte measuring probes I, II and, at the gas outlet of the solid electrolyte measuring probe II, a closely and thermally insulatedly connected CO₂ sensor III and O₂ sensor IV with a precedent gas dispensing device.

The solid electrolyte measuring probe I, the so-called q probe, contains as a gas sensor a unilaterally closed oxide ion conducting solid electrolyte tube which carries at its closed end which is towards the treatment gas and on the outside wall thereof the measuring electrode and opposite, on the inner wall, the reference gas electrode which is preceded by a catalyst path, and a thermoelement.

The solid electrolyte measuring probe II, referred to as the α probe, consists essentially of a bilaterally open oxide ion conducting solid electrolyte tube carrying on its outer wall the measuring electrode which is exposed to the treatment gas and opposite, on its inner wall, the reference electrode which is exposed to the completely reactive treatment gas, a catalyst path electrically heated and connected to the tube in gasproof manner and with a thermoelement, the measuring head of which is disposed in the catalyst path.

The solid electrolyte tube of the solid electrolyte measuring probe II is at its other end gas-tightly connected to a gas dispensing device while this is connected to the gas sensors CO₂ sensor III and O₂ sensor IV. The CO₂ sensor III and the O₂ sensor IV are secured in gas-tight fashion in an electrically heated casing tube at a constant temperature and formed as a compound tablet consisting of a CO₂ sensitive and an oxide ion conductive solid electrolyte, the measuring electrodes of which are exposed to the treatment gas which is fully oxidised and which is conducted out of the solid electrolyte measuring probe II and through the gas dispersing device, while the oppositely disposed gas-tightly separated reference electrodes are exposed to a catalytically reacted CO₂ and O₂-containing reference gas.

The throughflow of oxidation gas introduced into the gas dispensing device is, for a constant flow of treatment gas, maintained constant by a regulating choke or, in the case of a fluctuating throughflow of treatment gas, is controlled by a regulating valve connected via a controller which is responsive to a signal from the O₂ sensor IV.

In a second embodiment, the arrangement consists of a gas withdrawal tube which is corrosion resistant and which protrudes into the furnace space, a thermoelement protruding into the furnace space and, mounted in the immediate vicinity of the furnace wall, a measured value transmitter which contains the solid electrolyte sensors I and II and also, at the gas outlet and closely and thermally insulatedly connected, a CO₂ sensor III and an O₂ sensor IV with a precedent gas dispensing device.

The solid electrolyte sensors I, II are disposed in an electrically fired furnace which is connected to a temperature regulator, the thermoelement projecting into the furnace space being connected to the desired value input of the temperature controller. In the gas flow between the solid electrolyte gas sensors I, II there is an electrically fired catalyst path. The gas sensor I, the so-called q sensor, contains on an oxide ion conducting solid electrolyte tube, a reference electrode and opposite this a measuring electrode which is exposed to the treatment gas drawn out of the furnace space by suction. The gas sensor II contains on an oxide ion conducting solid electrolyte tube a reference electrode and opposite this a measuring electrode which is exposed to the completely reacted treatment gas. A catalyst is disposed in the reference gas space of both gas sensors I, II.

The outlet from the gas sensor II is connected in gas-tight fashion to a gas dispensing arrangement which is connected to the gas sensors CO₂ sensor III and O₂ sensor IV. The CO₂ sensor III and the O₂ sensor IV are secured in gastight fashion in an electrically fired casing tube of constant temperature and are constituted as a compound tablet consisting of a CO₂ sensitive and an oxide ion conductive solid electrolyte, of which the measuring electrodes are exposed to the fully oxidised treatment gas passed out of the gas sensor II and through the gas dispensing device while the oppositely disposed gasproofly separated reference electrodes are exposed to a catalytically reacted CO₂ and O₂-containing reference gas. The throughflow of oxidation gas introduced into the gas dispensing device is, for a constant flow of treatment gas, maintained constant by a regulating choke or, in the case of a fluctuating throughflow of treatment gas, is controlled by a regulating valve connected via a controller which is responsive to a signal from the O₂ sensor IV.

The method according to the invention, which applies the arrangement according to the first embodiment, is characterised in that the required measured process values are obtained from signals from the four gas sensors, gas sensor I (q probe) in the treatment gas delivering the oxygen partial pressure in the non-equilibrium of this gas at any given time, the gas sensor II (α probe) in conjunction with a heated catalyst path, furnishing a characteristic parameter for the remoteness of the gas phase situation from its state of equilibrium, the gas sensor III delivers a value for the level of carbon in the treatment gas while the gas sensor IV supplies an auxiliary value for a gas dispensing device disposed upstream of the gas sensor III in that the signals from the gas sensors I, II and the signal obtained by means of a computer unit from the signals of the gas sensors III, IV are adjusted to the empirically ascertained optimum value by varying the parameters of the heat treatment process, the signal from the gas sensor IV remaining constant thereby.

The method according to the invention, which applies the arrangement according to the second embodiment, is characterised in that the essential process values are obtained from the signals from the four gas sensors, the gas sensor I in the treatment gas delivering the current oxygen partial pressure in the non-equilibrium of this gas, the differential signal between the gas sensors I, II supplying a parameter characteristic of the remoteness of the condition of the gas phase from its state of equilibrium, the gas sensor III delivers a value for the level of carbon in the treatment gas while the gas sensor IV delivers an auxiliary value for a gas dispensing device upstream of the gas sensor III, the gas sensors I, II, with the aid of the control

circuit consisting of the thermoelements and the temperature regulator, being applied to the temperature of the treatment gas in that the signal from the gas sensor I, the differential signal from the gas sensors I, II and the signal obtained by means of the computer unit from the signals from the gas sensors III, IV being adjusted to the empirically ascertained optimum value by variation of the parameters of the heat treatment process, the signal from the gas sensor IV being maintained constant.

The explanation of the method and of the application of the arrangement in conjunction with the method will follow with reference to embodiments shown in the accompanying drawings, in which:

Figure 1 shows the cell voltage of the q-probe, plotted in relation to the partial pressure ratio $\frac{p(NH_3)}{p(H_2)^{3/2}}$ for 580°C and various degrees α of decomposition of the ammonia which remains after reaction of the atmospheric oxygen with ammonia to produce nitrogen and water vapour in a casing gas consisting of pure ammonia gas, air and 5% by volume carbon monoxide;

Figure 2 shows the cell voltage of the q-probe plotted in relation to the cell voltage of the α probe for 580°C and various concentrations of oxygen in the casing gas consisting of pure ammonia gas, air and 5% by volume of carbon monoxide;

Figure 3 shows the cell voltage of the α probe as a function of the degree of decomposition α of the ammonia in a gas which, in addition to ammonia, substantially contains inert gas, hydrogen and water vapour, at 560, 580 and 600°C;

Figure 4 is a factor for computing the concentration of carbon-bearing compounds in the heat treatment gas from the CO₂ concentration indicated by the CO₂ sensor at 580°C and for an oxygen concentration of 10.5% by volume as a function of U_q at various U_q values;

Figure 5 diagrammatically shows the structure of the arrangement according to the invention, in a first embodiment, and

Figure 6 diagrammatically shows the construction of the arrangement according to the invention, in a second embodiment.

As an example, let us consider the process of gas oxycarbonitration at 580°C with a gas consisting of pure gaseous ammonia containing 0.2% by volume water vapour, various additives of air with 1.68% by volume water vapour and 0.03% by volume carbon dioxide and an addition of 5% by volume carbon monoxide to the ammonia-air mixture.

In the case of a method according to the invention, the q-probe (gas sensor I) measures a cell voltage U_q dependent upon the partial pressure ratio $\frac{p(H_2O) + p(CO_2)}{p(H_2) + p(CO)}$ while the α probe (gas sensor II) measures a cell voltage U_α dependent upon the degree of decomposition α of the ammonia (as shown in Figure 5). In a second embodiment (shown in Figure 6), the cell voltage U_α between the measuring electrode of the gas sensor I and the measuring electrode of the gas sensor II is measured. Figure 1 shows the relationship between U_q and α and the partial pressure ratio $\frac{p(NH_3)}{p(H_2)^{3/2}}$. From this it will be seen that with the probes or gas sensors it is possible easily and directly to ascertain the nitration conditions and with the short response times of such probes or gas sensors it is possible quickly to adjust the optimum process conditions.

Figure 2 shows that by using the signals from the q and α probes (gas sensors I and II), it is also possible to determine the oxygen volume concentration $\varphi(O_2)$ of the treatment gas. With negligible errors, this diagram is also applicable to other process temperatures because the temperature dependency of the cell voltages of both probes or gas sensors, under the usual nitration conditions, amounts to less than 0.1 mV/K. Figure 3 shows U_α as a function of α at three different temperatures.

If it is intended, in parallel with the nitration, to carry out a carburisation on the metal surface of the workpieces to be treated, then the concentration of the carbon-containing gas component in the heat treatment space is of interest. To ascertain it, the treatment gas drawn from the α probe (gas sensor II) and fully reacted with excess oxygen is utilised so that carbon dioxide can always be determined from any carbon-containing gas components.

In order to adjust a quite specific residual oxygen content without measuring the volume or flow, then with a constant throughflow of the treatment gas drawn from the α probe (gas sensor II), the throughflow of oxidation gas, including air, is so adjusted that the O₂ sensor IV indicates exactly half the oxygen content of the oxidation gas. The volume of the treatment gas stoichiometrically reacted with the oxidation gas is then doubled. The reference electrodes of the q-probe (gas sensor I) and of the CO₂-O₂ sensor pair III and IV are expediently charged with air. For more exacting demands in terms of accuracy, the fluctuations in the CO₂ concentration of the air are a disturbance and then it is necessary to use a reference gas which has a constant and known concentration of CO₂. The quantity of matter in the treatment gas increases as the ammonia decomposes, so that the admixed carbon-containing gas becomes diluted. Further dilution occurs due to the supply of oxidation gas so that the CO₂ sensor III measures a smaller concentration that is adjusted prior to the heat treatment space and smaller than obtains in this space at the degree α of decomposition. The concentration effective in the heat treatment must be ascertained via an auxiliary factor F from the CO₂ concentration measured at the CO₂ sensor III. In the example of embodiment, with the addition of carbon monoxide and with the oxygen concentration at the CO₂ sensor III regulated to half the oxygen concentration at the CO₂ sensor III regulated to half the oxygen concentration of the oxidation gas, then when the gas used has an oxygen concentration of $\varphi(O_2)$ and a degree of decomposition α is present in the heat treatment space, the CO₂ concentration $\varphi(CO)$ acting during gas nitration is obtained from the CO₂ concentration $\varphi(CO_2)$ measured with the CO₂ sensor III more or less from the equation

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$$\varphi(\text{CO}) = F \cdot \varphi(\text{CO}_2)$$

$$\text{with } F = \frac{9.773 - 47.49 \varphi(\text{O}_2)}{0.9974 + 0.998}$$

- 5 In the equation, the CO₂ concentration of air has been allowed for at 0.03% by volume. 5
- Figure 4 shows a diagram for F as a function of U_q and U_a for a process temperature of 580°C and for half the oxygen concentration of air at the O₂ sensor IV.
- This has offered an example which shows that it is a simple matter to determine the most important
- 10 parameters for the nitration of workpieces in gas mixtures from the signals from three gas sensors I, II and III 10
- for a constant signal of an O₂ sensor IV:
- the gas sensor I (q-probe) signals whether the workpiece surface is oxidised or reduced,
 - the gas sensor II (α sensor) or in a second embodiment (according to Figure 6) the differential signal between gas sensor I and II signals the degree of non-equilibrium in the heat treatment gas,
 - 15 - with the signals from the gas sensors I, II it is possible to ascertain the partial pressure ratio $\frac{p(\text{NH}_3)}{p(\text{H}_2)^{3/2}}$ 15
 - and the oxygen volume concentration in the ammonia-air mixture used,
 - CO₂ sensor II delivers signals proportional to the volume concentration of the carbon containing gases at the workpiece and which are converted to this volume concentration by means of the signals from the gas sensors I, II.
- 20 In a practical application, it is sufficient for the signals from the gas sensors I, II and III to be recorded for a 20
- constant signal of the O₂ sensor IV and variation of the process parameters of the heat treatment and by means of the sensor signals to reproduce those process parameters which have been found to be optimum.
- Attention should further be drawn to the fact that at the catalyst in the α probe II or in a second embodiment according to Figure 6 between the gas sensors I and II when carbon monoxide is used as the carbon-
- 25 providing compound, only the adjustment of the water gas conversion equilibrium is accelerated which does 25
- not have any great effect on U_a on account of the values of the decisive equilibrium constant and concentration situation. If, on the other hand, some alcohol or a hydrocarbon is used, then noticeable effects can occur on U_a which are characteristic of the compound used. In these cases, U_a remains a signal for the degree of non-equilibrium, except that the relationships to the signals of the other gas sensors and to parameters
- 30 which have an effect on nitration, must be separately investigated empirically or arithmetically and taken into 30
- account according to the case in hand.
- Figure 6 shows the diagrammatic construction of the apparatus in a first embodiment. The q measuring probe 1 contains as a gas sensor I the solid electrolyte tube 2 of stabilised zirconium oxide which has at its closed end on the outside a measuring electrode 3 and opposite this a reference electrode 4. The reference
- 35 gas 5 is conveyed to the reference electrode 4 through a reference gas tube 6 in the front part of which there is 35
- contained a catalyst path 7, the reference gas 5 then flowing into the outside air via the interior of the probe. A thermoelement 8 is used for measuring the process temperature.
- As a gas sensor II, the α measuring probe 9 contains a solid electrolyte tube 10 of stabilised zirconium oxide which carries on the outside a first electrode 11 and opposite, on the inside, a second electrode 12, being
- 40 connected to a ceramic tube 13 which carries a heating winding 14 of nickel and a catalyst path 15. A thermo- 40
- element 16 serves to measure the temperature of the heating winding 14.
- The treatment gas drawn in through an aperture 17 in the probe sheath passes over heating winding 14 and catalyst path 15 into the interior of the solid electrolyte tube 10 and into the probe interior and then passes through the gas dispensing device 18 in which the treatment gas is reacted with an oxidation gas which is
- 45 regulated in throughflow through a regulating choke 19. 45
- The CO₂ measuring device which follows consists of the carrier 20 which has on its outer periphery a heating winding 21 and in its interior two gas sensors 22, 23 which divide the interior into two chambers separated from each other in gas-tight fashion. The CO₂ sensor 22 (gas sensor III) consists of a CO₂-sensitive solid electrolyte with a measuring electrode 24 and a reference electrode 25; with O₂ sensor 23 (gas sensor IV)
- 50 consists of an oxide ion conducting solid electrolyte with a measuring electrode 26 and a reference electrode 50
27. The completely reacted treatment gas flowing out of the gas dispensing device 18 into the measuring gas space is sucked out by a gas delivery pump 28. The reference gas 29 flows over a catalyst path 30 which is disposed in the reference gas supply line 31 and to the two reference electrodes 25, 27. The measuring probes 1 and 9 (gas sensors I and II) are fixed in the wall 36 of the heat treatment furnace, the electrical signal
- 55 processing is set aside spatially with the sub-assemblies 32, 33, 34, 35. The measuring signal from the probe 55
- 1 is prepared by the signal amplifier 32 for further processing, likewise the measuring signal from the probe 9 with the signal amplifier 34 and the measuring signal of the thermoelement 8 with the signal amplifier 33. The measured signals from the sensors 22, 23 (III and IV) are linked to one another in the electronic sub-assembly 35 to constitute a CO₂ signal and at the same time a variable is made ready for the regulating choke 19.
- 60 Figure 5 shows a second embodiment of the arrangement. 60
- Through a ceramic gas withdrawal tube 37 which passes through the wall 38 of the heat treatment furnace, treatment gas is drawn off and fed to the gas sensor I which contains a solid electrolyte tube 39 which is open at both ends. In its interior, this gas sensor I contains the measuring electrode 40 and opposite it, on its outer periphery, the reference electrode 41. After leaving the gas sensor I, the treatment gas flows through a heated
- 65 catalyst path 42 with a catalytically active heating winding 43 and then through a gas sensor II which also 65

contains, open at both ends, a solid electrolyte tube with an internal measuring electrode 45 and a reference electrode 46 fixed on its outer periphery and opposite the former. Both gas sensors I, II are located in a common heating furnace 47. The reference gas is fed to the two reference electrodes 41, 46 via a catalyst path 48.

- 5 The likewise possible sub-division of the treatment gas flow into two partial flows and catalytic reaction of a partial gas flow is disadvantageous in that the partial gas flow which is not reacted becomes chemically aggressive by virtue of its ammonia content, resulting in corrosion problems and pollution of the environment by harmful substances. From the gas sensor II, the treatment gas passes into the dispensing and mixing arrangement 18 in which oxidation gas is admixed through a regulating choke 19. The now completely
- 10 oxidised treatment gas flows into the CO₂ measuring arrangement, consisting of the CO₂ sensor III, a CO₂-sensitive solid electrolyte 22 and the O₂ sensor IV consisting of an oxide ion conductive solid electrolyte 23. The measuring electrodes 24, 26 of the gas sensors III, IV are exposed to the treatment gas which is passed through the entire measuring arrangement by the pump 28. The reference electrodes 25, 27 of the gas sensors III, IV are subjected to a CO₂-O₂ reference gas 29 which flows through a catalyst path 30. The signal U_a of
- 15 the gas sensor I, the signal U_a formed between the measuring electrodes 40, 45 of the gas sensors I, II and the signals from the CO₂ sensor III and O₂ sensor IV are amplified in the electronic sub-assemblies 49, 50, 51 and converted to uniform signals suitable for process control. The signal from the O₂ sensor IV furthermore serves to control the regulating choke 19.
- The temperature of the treatment gas is measured by the thermoelement 52 projecting into the furnace
- 20 space in the immediate vicinity of the gas withdrawal tube 37, prepared in a measuring amplifier 53 for further processing and then fed to an electronic controller 54 for regulating the temperature of the heating winding 47 which is connected to the thermoelement 55 which serves for measuring the temperature of the gas sensors I, II. The effect of the regulation is that the two gas sensors I, II accept the temperature of the treatment gas in the furnace space so that the same thermal conditions as in the furnace space will obtain at
- 25 these gas sensors I, II.

CLAIMS

1. An arrangement for monitoring heat treatment processes such as gas nitration, gas oxynitration, gas carbonitration, gas oxycarbonitration and carbonitration and nitride hardening with solid electrolyte gas sensors which have, opposite the solid electrolyte, a measuring or reference electrode, characterised in that this consists of four gas sensors, gas sensor I containing an oxide ion conductive solid electrolyte tube (2) closed at one end, in which there is also a thermoelement (8), the closed and contacted side of which is immersed into the treatment gas space, the reference electrode (4) being surrounded by a catalyst (7) located

30 in the reference gas line (6) and with an oxygen reference gas while the measuring electrode (3) is surrounded by the treatment gas, the gas sensor I consisting of an oxide ion conductive bilaterally open solid electrolyte tube (10), connected to a ceramic tube (13) which carries a heating winding (14) and a catalyst (15), both tube parts (10, 13) being immersed into the treatment gas space, the measuring electrode (11) being enclosed directly by treatment gas while the reference electrode (12) is enclosed by a treatment gas reacted via the

35 catalyst (15) and in that on the gas side the gas sensor II communicates through a downstream gas dispensing device (18) with two further gas sensors III, IV which are so disposed in a heated support (20) as to create two separate gasproof gas chambers, one having a CO₂-sensitive and the other an O₂-sensitive plate-shaped solid electrolyte (22, 23), the measuring electrodes (24, 26) being enclosed by completely oxidised treatment gas of the gas sensor II while the reference electrodes (25, 27) are enclosed by CO₂-O₂ reference gas (29)

40 initiated via the reference gas feed line (31) with catalyst (30) in the support (20), the signals from the gas sensors III, IV being interlinked via a computer unit (35), a regulating choke (19) preceding the gas dispensing device (18) in the process sequence.

2. An arrangement according to Claim 1, characterised in that the gas sensor I consists of an oxide ion conductive solid electrolyte tube (39) open at both ends and accommodated in a heating furnace (47) with a

50 thermoelement (55), the reference electrode (41) being enclosed over a catalyst path (48) disposed in the heating furnace (47) by an oxygen reference gas while the measuring electrode (40) is enclosed by a treatment gas flowing out of the heat treatment furnace through a gas withdrawal tube (37), the gas sensor II likewise consisting of an oxide ion conductive solid electrolyte tube (44) which is open on both sides and which is disposed in the same heating furnace (47), both gas sensors I, II being connected via a heated

55 catalyst path (42), the reference electrode (46) being surrounded over the catalyst path (48) by an oxygen reference gas while the measuring electrode (45) is enclosed in the treatment gas passed via the catalyst path (42), while on the gas side the gas sensor II communicates via the gas dispensing arrangement (18) with the gas sensors III and IV and in that a thermoelement (52) projects into the treatment gas which is connected via a temperature regulator (54) to the thermoelement (55) in the heating furnace (47).

3. A method applying the arrangement mentioned under Claim 1, having solid electrolyte gas sensors, characterised in that the essential process variables are ascertained from signals from the four gas sensors, the gas sensor I in the treatment gas indicating the current oxygen partial pressure present in the non-equilibrium of this gas, the gas sensor II representing a parameter characteristic of the remoteness of the gas phase condition from its condition of equilibrium, the gas sensor III delivering a value for the carbon level

60 in the treatment gas while the gas sensor IV provides an auxiliary variable for a gas dispensing device

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disposed upstream of the gas sensor III, in that the signals from the gas sensors I, II and the signal obtained with the aid of a computer unit and from the signals of gas sensors III, IV are adjusted by variation of the parameters of the heat treatment process to the empirically ascertained optimum value, the signal of the gas sensor IV being maintained constant in the process.

- 5 4. A method according to Claim 3, employing the arrangement mentioned under Claim 2, characterised in 5
that from the differential signal between the gas sensors I, II, it is possible to obtain a parameter characteristic
of the remoteness of the condition of the gas phase from its condition of equilibrium, the gas sensors I, II
being thereby, with the aid of the control circuit consisting of the thermoelements (52, 55) and the
temperature regulator (54), adjusted to the temperature of the treatment gas.
- 10 5. An arrangement as claimed in claim 1 substantially as described with reference to the accompanying 10
drawings.
6. A method as claimed in claim 3 substantially as disclosed herein.

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